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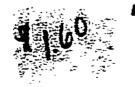
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COPROSION RESISTANT TITATION AND ITS ALLOYS

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THE THAISLATION HAS BEEN PREPARED IN THIS MAINER TO PROVIDE THE RECYESTENCISER WITH INFORMATION IN THE SIGHTEST POSSIFLE TIME. FURTHER EDITING WILL HOT HE ACCOUNTEDED BY THE PREPARING AGENCY UNLESS FULLY JUSTIFIED IN WRITING TO THE CHEEF, TECHNICAL DUZUMENTS ELABORICH IC., WILTO, FRAFE, CHO

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CORROSION-RESISTANT TITANIUM AND ITS ALLOYS by I. I. Kornilov

In addition to the widely known metals (copper, silver, nickel and cobalt, platinum, palladium etc) relatively new metals (titanium, zirconium, vanadium, niobium etc) in recent years began acquiring greater importance as corresion resistant materials.

The relatively greater availability in nature of titanium and its analogue zirconium and the high phys-chem. properties of these metals created favorable conditions for the development of methods for their obtainment in pure form. Perspectives appeared for the development of their industrial manufacture and application 1, 2.

In the nearest future the fields of application of Titanium wil' expand considerable. The last decade has seen greater successes in the manufacture of metallic Ti in the USA, England, Japan and other countries. In the USA, for example, in 1948 were obtained 3 tons of Ti, by 1957 the industrial capacity of titanium plants reached 27000 (cubic tons). The USSE also adopted and is successfully developing the industrial manufacture of metallic titanium.

The growth of the manufacture of metallic titanium in the USA is indicated by the following annual data:

In recent years the productive capacity of the titanium industry in various countries has increased considerably. There are available data on the volume of titanium manufacturer in 1957, in Japan (2441 t), in England (up to 2000 t) in France (up to 1000 t). There are indications that the total volume of world output of Ti in 1960 (without counting the USSR) will reach

100000 tons.

In spite of the greater importance of titanium in various branches of technology chiefly as a corrosion resistant material) it is still not in broad demand (it still does not find a broad market) because of the high price. A known hindrance is also the fact that for many important fields of application pure titanium does not possess sufficient strength.

Keeded are high-strength titanium alloys which as yet have not sufficiently developed and utilized. This partially explains why the titanium plants in the USA presently manufacture only 20 - 25% of the total productive capacity.

The composition of metallic titanium obtained by various methods is described in table 1.

The properties of metallic titanium are determined in relation to the degree of purity. Particularly sensitive to oxygen, nitrogen and hydrogen admixtures are the mechanical properties. These admixtures combined with titanium have a tendency of forming implantation type solid solutions and are very difficult to separate (remove) from it; they sharply increase the hardness, ultimate strength and considerably reduce the plastic properties of metallic titanium (table 2).

The most plastic (ductile) and the least strong appears to be the titanium obtainable by the iodide method or secondary purification.

Corresion Resistance of Fitanium

Pure titanium belongs to chemically active metals. The resistance of the metal to corrosion in an aqueous medium is connected with the electrode potential originating between the submerged metal and the standard hydrogen element.

A study of the corrosion properties of titanium in diluted sodium chloride solutions astablished a very interesting characteristic. Titanium with a

Table 1

Composition of Motallia Titanium Obtained by Various Methods

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Mothod n of change and a man	£				Com	positio	Composition, woight %	ht %			T
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Vitra-high purity	1	ı	0.02	ð	0.0	0.005	0000	0.0018		ŀ	

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ous Mothods	24 CM	2520 4025 5040
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tive of Ti Ob	Hardngan kg/mm	150160 100140 8050 5060
Mochanical Preportion of Ti Obtained by Various Mothodn	Mothods of obtaining 71	Hydridu-Calolum Magnoblum-Thormal Iodido Ultrahigh purity Buraau of Kinob USA

freshly cleaned surface immediately after plunging into a similar solution has a negative potential, which in the initial stage reaches 0.27 v.

With such a potential titanium would be exposed to rapid corrosion. However the electrode potential of the titanium in this medium increases with time in the presence of free oxygen access reaching a positive value of up to 0.40, 0.46 v. In this respect Ti appears to be an anlogue of Cr in which the electrode potential of pure Ti in various conditions of its surface in relation to the time of submersion and soaking in a 3-\$\frac{1}{2}\$ sodium chloride solution at 25° is presented in Figure 13. For all surface conditions Ti with time acquires a positive electrode potential. As the value of the potential increases the the titanium acquires passivity and become particularly stable against corrosion.

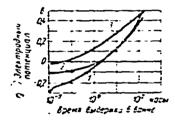


Figure 1 - Change in Electrode Potential of Ti in Relation to the Time of Submarsion in an Aerated 3%-NaCl Solution at 25°:

1 - Freshly polished, 2 - polished and soaked at room temperature; 3 - polished and heated in the air at 125°. a - electrode potential; b - time of soaking in Dath.

The chemical recolling of metallic titanium was investigated by many authors 1-4. The corrosion resistance of Ti in some instances exceeds the resistance of stainless steel and many other metals and alloys. The high corrosion resistance of the chemically active titanium is explained by the form formation on its surface of a thin oxide film, which as result of greater density and homogeneity protects the metal against further reaction with the cuter medium:

From this point of view it can be said that titanium appears to be stable in these media which not only destroy the protective film on its surface but promote its formation.

Titanium is stable against nitric acid (not fumic), nitrohydrochloric acid, to hydrochloric-nitric acid mixture (at room temperature), acetic acid, lactic acid, hydrogen sulfide, dry and moist chloric atmosphere and against many other media aggressive for ordinary metals.

A destructive effect on metallic Ti is produced by a number of mineral and organic acids: hydrofluoric, hydrochloric (concentrated), sulfuric and orthophosphoric acids; oxalic, formic (during boiling), trichloroacetic and trifluoroacetic acids. The aggressive medium for Ti appears to be also aluminum chloride, sodium peroxide, fluorine compounds, mixtures of chloride and fluoride salts of alkali metals etc.

It can be said, however, that the number of aggressive media relative to titanium is considerably smaller than the number of chemically active substances in contact with which it demonstrates high stability.

In recent years appeared new reports 5 - 12 devoted to the study of the corrosion characteristics of Ti in various media, including problems of its oxidation upon heating. The authors describe the corrosion registance of Ti in acids, alkalies, various salt solutions, sea and river water as well as a comparative investigation of the corrosion resistance of Ti, Zr and stainless steel in various organic media 5.6. For the purpose of experimentation they used Ti of the following composition: C 0.03 - 0.04%, $\frac{\pi}{2}$ - 0.05 - 0.06%, $\frac{0}{2}$ - 0.10 - 0.15% and, according to spectral analysis data, Fe not more than 0.10%, $\frac{1}{2}$, Cr, Fb, En, Cu of from 0.005 to 0.05%. Such a metal in the form of tablets was obtained by the powder metallurgy (ceramet) method by sintering and subsequent hot rolling. The experiments conducted for the purpose of determining the corrosion characteristics of Ti, obtained by the powder metallurgy method

and by the smelting method, showed practically identical characteristics. The authors, having investigated Ti in formic, acetic, lactic, oxalic and other acid media, established that it is stable in air saturated formic, lactic and other acids in all concentrations, but corrodes intensively in boiling 50%—solution of formic acid.

Considerable corrosion is observed in titanium in boiling citric acid and also in a diluted oxalic acid solution in spite of the fact that stainless steel experiences in it lesser corrosion and zirconium even lesser than that. Very high stability was demonstrated by Ti and Zr when subjected to aniline hydrochloride, chloroform, tritetraethylene chloride, tetrachloroethane and other media 6.

The report devoted to the formation of a protective film on Ti during its exposure to hydrochloric acid showed 7 that during the submersion of Ti in hydrochloric acid is formed a protective film. A denser and stronger film is formed in diluted acid solutions. It was established by the electronographic method that the protective film in the given case consists of betr-titanium hydride which disappears easily upon heating the metal in vacuo, after which the surface of the titanium again becomes active.

The report 8, devoted to the application of Ti and other alloys in various aggressive media, states that the corrosion resistance of titanium in chlorine, chloride solutions, in diluted hydrochloric acid solutions is considerably higher than that of Cr-Ni-stainless steel type 18-8.

The problems of oxidation of pure titanium and the mechanism of its oxidation during heating are discussed in reports 9 - 12, published in recent years. The effect of oxygen on titanium up to 300° and over and the related to it formation of varying in nature and oxygen saturated titanium layers are discussed. The processes of formation of oxide layers are subject to logarithmic and parabolic equations.

After lasting oxidation of Ti at temperatures of over 700°, according to the author, one should expect cracking of the skin of oxide scoria. The methods of electron diffraction of scaling resistance and corrosion resistance of titanium were investigated.

It was found that the stability of Ti is explained by the formation on its surface of an oxide film consisting of rutile (TiO₂) with solid cohesion with the basic metal on account of the secondary valence electrons. The author II investigated the formation of the oxide film in the form of rutile during the oxidation of Ti in an atmosphere of pure oxygen at 600 - 925°. It was found that the oxide film obtained at low temperatures (up to 200 - 400°) is thin and solid, and the film obtained at high temperatures (above 650°) is thick and porous. At such conditions of oxidation the oxide films lose their protective properties.

The report 12 devoted to the study of titanium oxidation at high temperatures discribes the study of the oxidation process of the metal in water vapors in relation to temperature. The range of temperatures was 700 - 1200°. The content of Ti used for this purpose was 96 - 98% (admixture not indicated). The rate of oxidation was determined by the method of overweight in dependence from temperature; testing time one hour. The scale obtained after the oxidation was subjected to m-ray analysis.

Table? brings data regarding the increase in weight of the vitanium species in the process of heating in the air and in water vapors (in ng/cm^2) in relation to temperature.

The data in the table indicate that in water vapors the oxidation intensity at 900 - 100° is considerably higher than in the air; at 1000° and over this difference, at a very high rate of both oxidation processes. Is mixed out to a large extent and at 1200° the intensity becomes almost uniform.

A study of the nature of oxides showed that in conditions of oxidation in

101-140/1+2

Table 3

******	:		?emper:	sture '	°C	
Atmosphere	700 ;	800	900 '	1000	. 1100	1200
Air	1.0	2.1	5.4 !	13.8	36.0	70.0
Later vapor	2.9	7.6	13.2 ;	21.8	39.0.	75.1

in water vapors, the scale consists only of TiO₂, and in an air atmosphere in the scale are formed all three titanium oxides: TiO₂, Ti₂O₃ and TiO in the outer, central and internal layers of the scale respectively.

In connection with the corrosion resistance of titanium in various wedia attention should be called to a very important circumstance connected with the explosive properties of tit nium. This property is possessed also by the titanium analogue - zirconium. The explosive tendency of pulverulent Ti and Ir is discussed in report 13. It is noted that the spontaneous combustion temperature of a dry Ti-powder varies from 300 to 600°.

Titanium powder, sponge, dust, shaving can ignite easily from a spart or small flame. A great influence on the acceleration of the process of spontaneous combustion and explosion is exerted by moisture. That is why titanium powder should be stored without any traces and access of moisture, best of all in a neutral atmosphere medium, which cannot be nitrogen or carbon dioxide because titanian reacts also with them. The most reliable medium is helium or argon. Mater should not be used for extinguishing hot Ti (there may be an explosion of greater force). Inert gases for putting out Ti-fire are used only in conditions when the access of free air is cut-off. The extinguishing is best of all done by covering the flame and the space around the burning metal with some kind of dry powder (calcium fluoride, graphite, slaked lime).

Still another characteristic of titanium has been observed: sudden (unexpected) explosions during its lasting contact with fuming nitruc acid 14.

K O D & K - S - K E E

Such explosions are due to the simultaneous processes leading to explosive reaction. They can take place under the following conditions:

- internal stresses in titanium can rapidly remove the protective oxide
 film from the surface;
- 2) penetration into the small surface cracks of natric oxides which may begin acting catalytically and accumulate a rapid action of nitric acid;
- 3) the presence of small cracks on the surface of the metal, where the nature oxides concentrate, thus subjecting the metal to rapid oxidation. A study of titanium samples after such explosions shows the presence of local flashing-off points and the absence of the liquid phase in other points.

In this connection the studies of these phenomena are carried out in vessels isolated by covers and special protective partitions.

It should be mentioned, that this pertains only to pure metals. These phenomena are not observed in metal alloys prepared on the base of these pure metals.

Metallochemistry of Titanium Alloys

With all these favorable properties, high corrosion resistance of pure Ti in many appressive media, it is difficult to assume that titanium in pure form will find broad application in industry, including also the chemical industry. In order to use titanium as atructural material, for the manufacture of various products it must possess high mechanical properties in addition to the corrosion resistance. It requires high ultimate strength as sufficient ductility, high heat— and spalling resistance. As was shown, titanium in pure form has low atrength, and titanium with increased context of admixtures even though it possesses greater strength but it has no high ductility properties.

These circumstances prompted the development of investigations into the field of finding new titanium alloys and utilization of same in industry. In

the scientific way of exploring and oreasing new high quality titanium alloys the chemical relation of Mi with elements of the periodic system is of great importance. These problems are investigated by the metallochemistry of titanium and its alloys. A number of reports on metallochemistry and, particularly, on the metallochemistry of titanium alloys 14-18 discuss the problems of the reaction of metals with the elements of the periodic system. It is shown that the nature of the reaction is determined by the crientation of the elements in the D. I. Mendeleyev's periodic system with respect to the titanium 18. With the elements of the I and II groups (with the exception of Be) titanium does not react at all, with a number of elements of the VI - VII groups it forms ionic or covalent bonds with the elements of the remaining groups it forms limited solii solutions with metallic compounds or continuous solid solutions. The latter are obtained during the reaction of Mi with its analogues (Zr, Ef) or with elements oriented in the neighborhood of T1 (V, Xc, Ta, Yo).

Ine important elements for the development of titanium alloys appear to be:

from the limitedly soluble and numerous metallic compound forming elements
copper, beryllium, boron, aluminum, silicon, germanium, tin, chromium, mangan
ese, iron etc; from the metals, forming with it continuous solid solutions
mirconium, vanadium, molybdenum and miobium.

A greater number of elements, firming with titanium limited and continuous solid solutions, requires the study of the nature of the reaction between Ti and many elements, and the knowledge of a greater number of structural diagrams of simple and complex titanium systems. They should serve as the scientific basis in the development of new titanium alloys of practical application.

Each metal, used for the development of new alloys, can serve as an example to prove that there are important systems determining the bable compositions of alloys of those metals. Such systems can be called basic metallic systems serving as basis for many alloy compositions.

In this respect titanium should have a number of basic systems on the basis of which are developed investigations for the purpose of finding new titanium alloys. Such systems include combinations of titanium with important elements forming with it continuous or limited solid solutions or high-melting compounds. The number of these basic systems should include titanium-zirconium 17, titanium-rluminum 18, titanium-tin and so on.

The idea of strengthening metals at the expense of their multicomponent solid solutions 20 for the purpose of developing new high-strength titanium alloys led to a decision of simultaneous alloying the solid —Ti solution with aluminum, chromium, silicon, iron, boron etc. The selection of concentrations of these elements was determined by their maximum solubility in homologous binary titanium systems. In selecting the components consideration was also given to the availability and nonavailability of the alloying elements. As is known, the selected elements — Al, Cr, Fe and Si appear to be available and not too costly.

In this way a six-component solid solution of -titanium with aluminum, chromium, silicon, iron and boron was selected as the base for new heat-resistant titanium alloys. The threshold concentrations of these elements were calculated in such a way as to have the six-component alpha-solid solution of titanium as the base for the new alloys. The consequent investigation of the effect of Al, Cr and other elements on the limit of distribution of solid solutions in this complex system and on the change of properties of these solid solutions, established the optimum compositions of a number of new compounds which are of practical interest.

New High Strength Fitanium Alloys

Theoretical and experimental investigations led to the development of new high-strength titanium alloys with high ultimate strength values at room and

higher temperatures of up to 600 - 650°. Table 4 describes the basic characteristics of these alloys. Figure 2 and 3 show curves for the ultimate strength and percentage elongation of rupture and in relation to temperature for new experimental titanium alloys. These alloys were named T-3, T-4, T-6, T-8, T-9 and T-10. The obtainment of the listed alloys was developed by the mathod of arc-smelting.

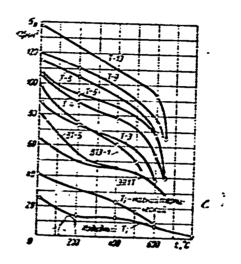


Figure 2 - Ultimate strength of New High-Strength Titanium Alloys in Relation to Temperature.

a - magnesium thermal; b - iodide.

The high (ultimate) strength properties considerably exceeds the strength of Ti, aluminum alloys, many alloyed and stainless steels. The plastic (ductile) properties of the new alloys are sufficient for their application in the role of structural materials for various objects.

The corrosion properties of titanium alloys have been investigated in sufficiently 4. There are only several reports devoted to problems of corrosion of 7i and its base alloys and another one - to the oxidation resistance of titanium-base alloys. The corrosion resistance of titanium and its alloys must investigated in various chemical media, the changes in the 7i-potential in various solutions were determined and the mechanism of formation and the

Knahanioal Propartion of Now Titanium Alloyn at Room Tomporaturo in Comparinon With the Propartion of Pure Titanium and Industrial Titanium Alloyn Tublo 4

			DOTTE HATTING TO THE PROPERTY OF THE PROPERTY	Denty mar.		
	To modulus of	£,	Proportion at	20°		-
namen of Alloyn	oluntjoity kg/mm	us tim. atrength kg/mm	Blongat.	-) %	stron;th kgm/on?	Spootfic wolcht & Com
	Proportion of titanium and existing alloys	ntum and ext	oting alloyn			
Tithnium typo TKi-O VP-5 VPX-1 OT-4 T-4 (obtained by the	11300 11000 11000 00011	80 8027 7272 7885	30 12-125 15-40	67.0 30-145 85-146	3.50 2.50 2.50 3.50 3.50	4444 ถ้นถ้า
mothod)	i	105115	1015	2030	34	4.45
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composition of the protective films were investigated. During the study of the change in the potential of Ti, first passivated in water, repeated passivation was revealed in a 24-solution.

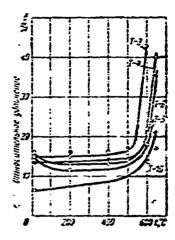


Figure 3 - Percentage of Elongation of Rupture of New High-Strength Ti- 'lleys in Relation to Temperature.' a - elongation per unit length.

The film formed during repeated passivation, during heating to 100°, remains in tact, while the primary film formed in an air-saturated 0.01% NaCl-solution disintegrates upon heating to 40°.

Electron-diffraction study of the compositions (constitutions) of the primary and secondary films showed that while the secondary film contained titanium hydride (TiH2) plus other titanium compounds, apparently TiO, the primary film consists only of TiH2. The effect of various elements on the corrosion resistance of Ti was also investigated. A substantial corrosion resistance of Ti in sulfuric, hydrochloric, phosphoric saids is observed during the alloying of Ti with 30% molybdenum. Titanium alloys of this series when exposed to the mentioned acids possess greater stability than the well known nickel/molybdenum alloy of the Eastelloy type.

The oxidizability of binary Ti-Cr, Ti-Al and Ti-Be alloys was investigated at 300 - 900°. The investigation results showed that the Ti-Be alloys demon-

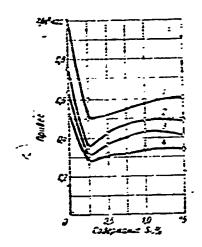


Figure 4 - Rate of Oxidation at 700° of a six-component titanium alloy 7-4 in relation to the Si-content: 1 - within 25 hours; 2 - within 50 hours; 3 - within 75 hours; 4 - within 100 hours. a - overweight.

strated maximum oxidation resistance. At 700 and 900° the oxidation curves (after change in weight) for the Ti-Be alloys have a parabolic character and with the increase in the content to 6% the rate of oxidation decreases considerably. Ti-Or alloys (up to 25%) show a drop in their oxidation resistance at 700 - 900°. Alloys with 20 and 25% of Cr have a somewhat higher resistance than pure titanium. The addition of Al to Ti also reduces the oxidation resistance of Ti at 500°. But at 700° with an increase in the Al-content its stability increases. The oxidation resistance at 700° increases especially upon increasing the Al-content to 15%. According to other information, maximum oxidation résistance up to 1100 - 1150° is demonstrated by Ti-Al alloys corresponding to the Ti-Al compound and according to the structural diagram of this system in the zone of the gazma-phase within the composition limits of from 36 - 42% of Al.

The series of six-component experimental titanium alloys was investigated to determine the effect of Al and Si on the heat resistance (resistance against

oxidation) of the T-4 alloy, obtainable by the powder metallurgy method. The oxidation was investigated at 700° by the method of overmeight on cylinarical samples; duration of the experiment 100 hrs.

The results obtained by studying by the overweight method made it possible to calculate the rate of oxidation of the alloys in relation to the variable content of all ranging from 4 to 12% and Si from 0 to 1.5%.

In proportion to the increase in the aluminum content the rate of alloy oxidation at first (up to 3 - 4%) increases, and above 4% it decreases smoothly and the minimum rate corresponds to a six-component alloy with 12% Al.

The effect of Si na rate of oxidation of a six-component alloy was found to be different from the effect of il. The five-component alloy T-4 (without Si) has a high rate of oxidation. In addition of up to 0.25% of Si sharply reduces the rate of oxidation of this alloy; a further rise in the Si content to 1.5% leads to a slight change in the rate of oxidation (see Figure 4). It can be concluded from these data that aluminum as well as silicon do evert in influence on the increase in oxidation resistance of the six-component T-4 alloy at 700°.

Utilization of Fitanium and its Alloys

Pitanium and its alloys find broad application in various branches of technology. They find maximum use in aviation and in rocket technology. In these fields the combination of high strength and small specific weight is of special importance. According to the report of the representative of the English Company "Imperial Chemical Industries" about 90% of the titanium produced in England goes for aviation. The titanium with time will prove to be the irreplaceable material for satellites and toher cosmic devices.

Titanium finds considerable application in naval shipbuilding. Thanks to its high corrosion resistance in sea mater titanium and its alloys are of

greater value for the sheathing of ships, submarines, torpedoes and for other purposes in sea transportation.

Titenium and its alloys should find broad application also in other branches of industry. This permains first of all to the chemical industry where the use of tiatnium and its alloys as high-strength and corrosion resistant materials has greater perspectives.

Titanium and its alloys are used in the manufacture of various components of chemical machines, which are exposed to the effects of aggressive media (pipes, fittings, valves, vents, screens, different parts of pumps, etc). A greater number of the parts is manufactured from pure Ti because in many instances it appears to be more corrosion-resistant than its alloys and furthermore, from it, it is easier to make many objects by various types of machining and welding than from its alloys.

Pitanium is used for blades and housings of centrifugal pumps used for "pumping of various organic acids, chlorifus, 3.55 hydrochloric acid solution and dry chlorine. In these objects titanium can operate for several years, while the Mi-Cr-Mo-alloys previously used for such purposes had a service life of less than one year.

Fitanium injectors, operating at high steam and liluted hydrochloric acid velocities, can withstand the load for more than 2.5 years without any noticeable traces of corrosion while case iron injectors were being put cut of commission within a period of three months.

Forged titanium valves are used for intake pipes functioning for the feeding of aggressive liquids under a pressure of up to 2 kg/mm². They operate for more than 1680 hours without replacement. Valves made of stainless steel had to be replaced after 70 hrs of operation. In this way, titanium valves are almost 20 times more durable than stainless steel valves.

Mixing druns for the mixing of chlorine dioxide, lined inside with titanium sheets, within one year showed no noticeable corrosion, while Ni-Or-No alloys operating under similar conditions required replacement after five hours of operation.

Fitanium wire screens possess high corrosion resistance. They are employed in the role of filters for the filtering of calcium hypochlorite crystals in the presence of moist chlorine at a pressure of up to 2.5 kg/m 2 .

Titanium and its alloys are of greater importance in the manufacture of high speed ultracentrifuges where a reduction in the rapidly rotating mass is very important.

Pipes made of titanium and its alloys are used in the role of heat exchangers for the distillation of nitric soid vapors and for other purposes. Because of the danger of employ on of titanium in nitric acid it is advisable to use alloys of titanium with aluminum.

Various objects made from pure titanium and certain alloys can be manufactured by rolling, puccesing and other means of mechanical machining, intricate parts can also be manufactured. Sesting or by the powder metallurgy method.

These examples are far from sufficient in describing the fields of application of Ti and its alloys in the chemical industry. Because of the scant knowledge regarding the corrosion resistance of titanium alloys it is difficult to foresee the peropertives for their utilization in the role of corrosion-resistant materials, which are wasted away in the different composition of the already made or being made new titanium alloys.

The scientific-research institutions and the factories of the chemical industry should conduct experiments on the utilization of new titanium alloys in the role of corrosion-resistant materials in various devices and installations operating in aggressive or its.

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